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Monitoring of natural sulfur compounds in the atmosphere of Kosan, Cheju during the Spring of 2001

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Abstract

The concentrations of dimethylsulfide (DMS) and carbon disulfide (CS₂) were measured concurrently with relevant environmental parameters at Kosan, Cheju during April 2001. The mean concentrations for these two compounds determined during the whole study period were 18.7 and 6.1 pptv, respectively. Results of our analysis indicated that relative temporal variations between DMS and CS₂ can be best described by grouping the whole period into three different periods that reflect the variable transport patterns of air masses into the study area. (Periods I, II, and III denote: 5~14, 15~20, and 21~26 April.) It appeared that DMS behaved very similarly to CS₂ during periods I and III with relatively high concentrations of CS₂ and DMS. For both of these two periods, continental air masses were introduced along with fairly high wind speeds of above 9 m s⁻¹. By contrast, a notable reduction in both DMS and CS₂ levels during period II was apparent, accompanied by the inflow of a well aged marine air mass. Most of these variabilities were hence explained in terms of an interplay between source/sink processes and air mass transport. The sea-to-air flux of DMS, when estimated using our measurement data during this study period, was 4 μmoles m⁻² d⁻¹.

Key words: dimethylsulfide, carbon disulfide, temporal variation, natural emission, S chemistry

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1. Introduction

In an effort to elucidate the relationships between the atmospheric environment and earth's climate, the study of natural sulfur chemistry has been considered as one of the most intriguing subjects in atmospheric chemistry [e.g., Charlson et al., 1987]. Similarly to most airborne pollutants, sulfur compounds are released into the earth's atmosphere as a result of both natural and anthropogenic processes [e.g., Spiro et al., 1992]. It is well known that the single sulfur compound, SO_2 represents almost the sole form of sulfur gases produced by various man-made activities. By contrast, a number of reduced sulfur gases (including DMS, H_2S , CS_2 , COS, CH_3SH , etc.) are identified as major components of the natural sulfur chemistry [Andreae, 1990]. It is also recognized that the formation of those sulfur compounds can be made via diverse pathways: for example, the production of DMS, which constitutes the dominant component of natural sulfur gases, occurs in surface seawater as a metabolic byproduct by of phytoplankton [Dacey and Blough, 1987] or as a result of their destruction via zooplankton grazing [Dacey and Wakeham, 1986].

Being geographically located in a relatively remote area, the Kosan district of Cheju island, Korea has been investigated intensively for the proper assessment of both the absolute and relative importance of major source processes that exert controls across the Far Eastern countries like China, Japan, and Korea [e.g., Carmichael et al., 1997; Hayami and Carmichael, 1997; Kim et al., 1998]. If one acknowledges the possibility that large quantities of S and N compounds can be transported via westerlies from major source regions like China, measurements of reduced sulfur compounds at this strategic site are expected to provide valuable information concerning the relative significance of the local or regional sulfur budget. The present study, while being intended to investigate the fundamental aspects of the sulfur cycle at Cheju island, incorporates into a large-scale project known as the Aerosol Characterization Experiment Asia (ACE-ASIA). Hence in accordance with the intensive study plan for the project, an exploratory field study was undertaken to measure the concentrations of two reduced sulfur compounds (including DMS and CS_2) and relevant environmental parameters from Cheju Island for a large part of April, 2001. Our acquisition of the new data sets, collected on the basis of continuous measurements at short-term intervals, is expected to allow a better description of S chemistry at Cheju island in conjunction with our previous measurements of DMS in the same study site but over a more extended time period [Kim et al., 2000].

2. Methodology

The environmental and meteorological conditions at the Kosan site (Fig 1) have been described in detail from numerous studies made previously [e.g., Chen et al., 1997]. Studies of AQM at the Kosan district have been facilitated by the presence of the Cheju Meteorological Station (CMS); CMS has the responsibility for constant monitoring of the most important meteorological parameters in the region. The collection and analysis of S gases in the air were made by an on-line GC system interfaced with a Pulsed Flame Photometric Detection (PFPD) technique. The application of this continuous measurement technique has been possible by modification of the procedures of Swan and Ivey [1999] introduced previously.

The methodological approaches used in this study can be summarized briefly as follows. The collection of each air sample was made for a total duration of 15 mins. Air samples were drawn at a flow rate of 240 ml min⁻¹ through a PTFE sampling line stretched out on the top of a trailer-type field laboratory. The ambient air drawn via this sampling system was trapped cryogenically to focus S gases without allowing the penetration of H₂O vapor into the GC system. To deliver those trapped S gases into the GC column, the sampling line was heated at 35 °C. The combination of our GC/PFPD system offered many advantages (e.g., good detection limit, low price, compactibility, etc.), similar to those of other well-known techniques like the S chemiluminescence detection (SCD) method [Eckert-Tilotta et al., 1992; Ivey and Swan, 1995; macTaggart et al., 1999]. The detection limit for the system was found to be 0.02 ng of S which corresponds to about 2 pptv of mixing ratio (at total sampled volume of ~4 l). The concentrations of two sulfur compounds, determined originally at 20 min intervals, were all converted into hourly data sets for the purpose of comparative analysis with other concurrently measured environmental parameters. This procedure hence led to the sum of around 360 hourly data points for both S gases. These data were then examined for their inter-compound relationships and for their association with diverse environmental parameters investigated concurrently at the CMS.

3. Results and discussion

3.1 Synopsis of S-gas distribution characteristics at Cheju Island

As part of the period set for intensive study for the ACE-ASIA project, the analysis of DMS and CS₂

was made during the spring season of 2001 (5 ~ 26 Apr.). Using our measurement data, the time series plots for both DMS and CS₂ are presented in Fig 2. (For reference, local time scale was adopted for Figures and Tables presented in this work.) The distribution of both compounds seemed to be highly variable and diverse during the whole study period. The concentration of DMS fell in the range of below detection limit (DL) to the maximum of 107 pptv, while that for CS₂ peaked at 110 pptv. In recognition of the abundance of lower bound concentration data (especially in the case of DMS) and their controls on the computed mean value, we substituted the value of zero for those measured as below DL. Whereas DMS concentration below DL was summed as 20 cases out of 358 data points (~5.6 %), that for CS₂ showed 42 out of 356 data points (11.8 %). The peak concentration of DMS (107 pptv) was seen at 19:00 on 4/24 (JD=115), but that for CS₂ (110 pptv) was observed much earlier at 09:00 on 4/14 (JD=105).

Examination of inter-compound relationships between DMS and CS₂, especially in terms of their temporal distribution and of air-mass transport patterns (explained below) indicated that the whole measurement period can be classified into three different periods as follows: (1) Period I: 4/5 (JD=95) ~ 14 (JD=105); (2) Period II: 4/15 (JD=106) ~ 20 (JD=111); and (3) Period III: 4/21 (JD=112) ~ 26 (JD=117). Our grouping scheme of data sets indicates that relative temporal patterns are exceptionally dynamic across different periods (refer to the results of linear regression analysis in Fig. 3). For the period I, changes in their concentration levels tended to occur in an identical direction but with large variability. It was noticed that the concentration level of CS₂ during this period was the largest of all three periods. By contrast in period II, both compounds showed the least mean values for all periods; however, the pattern was reversed so that the DMS concentration decreased, while CS₂ concentration increased (Fig. 3). The uniqueness of this period may be explained by exceptional five-fold decrease in CS₂ concentration with only a slight reduction in DMS concentration relative to period I. At last in period III, their distribution patterns returned to the positive trend, as seen in period I. In this period III however, differences in the mean concentration levels between DMS and CS₂ are much larger than in period I, despite fairly strong correlation between the two compounds.

Because DMS concentrations were investigated previously at this Kosan site by our study group [Kim et al., 2000], our present results can be used to derive the general distribution characteristics of DMS in the study area. In our previous study, the DMS levels measured across fall, winter, and spring (1997-1998) exhibited significant differences across seasons. The DMS levels, while substantially higher than

those observed from the present study, showed the minimum seasonal mean value of 50 pptv during fall. Its concentration then showed an approximately a two-fold increase across fall, winter, and spring. The mean DMS levels for the spring season hence approached values as high as 190 pptv. Although several-fold differences in DMS levels between the present and previous study may not be explained with the data available, large differences in observed DMS concentration between the two studies suggest that the factors controlling source/sink relationships of DMS might have changed significantly between the two study periods.

3.2 Relationships between S-gas distribution and meteorological conditions

In order to explain the behavior of both S gases, we made concurrent measurements of the basic environmental parameters. While the mean temperature measured during the three study periods changed moderately from 12.9 to 14.6 °C, that for wind speed exhibited a rather dynamic variation with a minimum of 6.19 (period II) to a maximum of 9.45 m s⁻¹ (period I). Examinations of environmental parameters measured across three different periods indicated that the results for period II can be distinguished from others by slightly enhanced values for temperature and RH but reduced ones for wind speed and precipitation (Table 1 and Fig. 4).

To further study the factors affecting the distribution characteristics of S gases, we conducted a correlation analysis between S gases and environmental parameters (Table 2). When we looked closely into the correlation results between the wind speed and S gases, the results were highly contrasting among different periods. Most noticeably, the results for periods I and III contrast highly with those of period II, especially in terms of their correlation strengths for both between DMS and CS₂ and between S gases and wind speed. The presence of generally strong correlations in both periods I and III may hence be explained as part of wind rise effects. The close linkage between DMS and wind speed in fact appears to be prominent during certain days (such as JD=101, 110, and 115), when high DMS concentrations coincided with wind speeds over 10 m s⁻¹ (Fig 4). This observation directly indicates the possibility that atmospheric DMS levels observed during this study period were influenced largely by emission from surrounding seas to the atmosphere.

To further explain the behavior of these sulfur gases and their relationships with environmental conditions, we examined the movement patterns of air masses during each period (Fig 5). As period I

covers about one half of the whole study period, the results of back-trajectory analysis are diverse. The air masses tended to be transported into Cheju via their passages through: (1) the Russia and the East Sea (Sea of Japan), (2) mainland China and the Yellow Sea, (3) the NE China Sea, and (4) the NW Pacific. As such, many diverse processes must have been operating in controlling S-gas behavior during this period relative to the other periods. By contrast, the patterns for the period II are much simpler than for period I. During this period, air masses were rising most frequently from the northeast China Sea or within the Yellow Sea. In addition, it was also seen that air masses were coming across the Yellow sea after passing over China or across the East Sea (Sea of Japan) from Russia. The strongest homogeneity however appeared to exist during the study period III when air masses originating from northern China were passing across the Korean peninsula into the Kosan area. Hence, we suspect that the air masses entering the Kosan area during this period III might have been sustained over the Korean peninsula for a relatively long time.

Comparison of wind rose patterns in conjunction with the back-trajectory analysis between the different study periods also indicates trends that are quite consistent. It is interesting to note that the results of our analysis generally comply with a complicated nature of different source processes for the two S compounds. While the predominant fraction of atmospheric DMS is of natural (marine) origin, it is unlikely in the case of CS₂. Hence contrary to DMS, CS₂ is reported to maintain high average continental surface layer concentrations (35-120pptv) relative to marine surface layer air (2-18 pptv) [Seinfeld and Pandis, 1996]. Similarly to these authors, Watts [2000] also distinguished spatial distribution patterns of CS₂. It may hence be reasonable to suspect that the occasional enhancement in CS₂ levels during our study periods are due to anthropogenic influences which can be introduced along with air masses from the inland areas.

As the inflow of air masses occurred in various manners during the study period I, winds were also rising from almost all directions (Fig 6). Observations of the highest CS₂ level during period I suggest that this period was affected rather significantly by man-made processes. In fact, the occurrences of enhanced CS₂ value (e.g., maximum of 110 pptv) coincided with backward trajectories on 4/12 and 4/13, when low altitude air arrived at Kosan directly across the east coastal area of China (see Fig 5). However, moderately high DMS levels maintained during this period may be ascribed to its enhanced emissions under strong winds. In period II, slowly moving winds from the SE or W dominated relative to

other directions. It was noted that the concentrations of DMS during this period II were reduced moderately relative to the other periods, while the levels of CS₂ decreased notably. The contrasting trend between DMS and CS₂ concentrations in this period II seems to be associated by and large with the characteristics of air masses transported into the study area during this period. The results of back-trajectory analysis suggest the possibility that the distribution of S gases were affected by well aged marine air isolated from continental sources. The dramatically reduced CS₂ level may hence be explained by the dominance of natural source processes, while the minimum mean DMS concentration around 14.7 pptv may be due to less emission at low wind speed. During period III, winds were rising dominantly from a northerly direction: this result may be comparable to those observed as the typical seasonal pattern for the study area [e.g., Chen et al., 1997]. During this period both S compounds showed higher concentrations in the fast moving northerly winds. Hence, the rise of CS₂ levels during this period III may in part be accounted for by the influence of inland source processes. The mean concentrations of CS₂ during period III (4 pptv) increased two times from the least mean value of 2 pptv during period II. It should however be noted that the observed DMS concentrations during this period III were the highest of all the three periods. As stated previously, an intense gas transfer mechanism driven by high wind speeds and relatively low oxidant levels (as discussed below) during period III are suspected to help elevate atmospheric DMS concentrations.

3.3 Short-term variabilities of DMS and CS₂ during the study period

In the previous section, we described the temporal distribution patterns of the two S compounds in terms of their relative relationships across the whole study period. Similarly to such an approach, their distribution patterns over a short-term period (such as over 24-h scale) can also be useful to assess the general information concerning the environmental behavior of the two S compounds. As a direct means to examine the relationships between S compounds and basic meteorological parameters, we first compared the diurnal variabilities of temperature, wind speed, and RH. The results of our analysis are compatible with the general expectation that temperature and wind speed exhibit a notable enhancement during the daytime, while RH values behave in an opposite direction. By contrast, the S gas data sets are found to be much more complicated with the appearance of diverse features across different study periods.

According to the overall results presented in Fig 7, both compounds showed high concentrations during the daytime relative to nighttime for the whole study period. However, when their diurnal variations were again examined individually for each study period, the previously observed patterns for each period were seen to be no longer consistent. For study periods I and II, daytime values for DMS appeared to be slightly enhanced compared to the nighttime counterpart. On the other hand, the results for period III are clearly distinguished from the others in that DMS exhibited a clear nighttime enhancement. Unlike DMS however, the diurnal variability of CS₂ appeared to be most prominent during period I.

Because the three periods are clearly distinguished from each other in various respects, the causes of their diurnal variations may have to be assessed separately rather than as a whole data group. In general, the diurnal variation of DMS can be explained by an interplay between its physical mobilization (emission to the overlying free troposphere from surface seawater and subsequent transport to the boundary layer (BL)) and the chemical loss (via oxidative reactions with radicals such as OH and NO₃). In the remote marine BL, the diurnal variation is hence expected to be controlled mainly by OH oxidation. According to Shon et al. [2001], the contribution of NO₃ is less than 15% of total DMS oxidation in the remote marine BL where the NO_x levels tend to be present near its detection limit (e.g., <5 pptv). If we assume that the sea-to-air flux of DMS and its vertical transport at the study site did not change significantly over the diurnal scale, the amplitude of diurnal variation can be affected mainly by the oxidative reactions. It was in fact found that NO_x levels measured at the Kosan site during ACE-ASIA in April 2001 were up to two orders of magnitude higher than those typically found in the remote marine BL. Hence, large variabilities in oxidation capacity during nighttime (NO₃) appeared to exert significant controls on the diurnal variation patterns of DMS during each study period. The contribution of NO₃ oxidation was computed to be larger by about 50% on average than that expected from remote sites, resulting in a short DMS lifetime (e.g., less than a half day rather than one day). The result of this could produce the two distinct features in periods I and II (i.e., the DMS peak in the late afternoon and a gradual decrease even after sunset) which can be explained by enhanced NO_x levels at the sampling site. Similarly to our observations in periods I and II, the importance of NO₃ radical on relative enhancement in daytime DMS concentrations has also been suggested by Kouvarakis and Mihalopoulos [2002]. The enhanced DMS levels in the late afternoon for period III hence may be explained by relatively low NO_x

levels (e.g., decreased by an order of magnitude during this period), compared to the other ones (I-II). Consequently, this reduced NO_3 level during period III might have helped, at least partially, maintain the highest DMS level of all the three periods under comparison.

The mean flux for DMS during the whole study period, if estimated using a mass-balance photochemical-modeling approach described by Shon et al. [2001], was $4.0 \mu\text{moles m}^{-2} \text{ day}^{-1}$. The estimated fluxes during periods I through III were estimated to be 4.4, 3.6, and $4.9 \mu\text{moles m}^{-2} \text{ day}^{-1}$, respectively. In the mass balance equation, the time rate of DMS change is dependent on sea-to-air flux and DMS removal (via reactions with OH and NO_3). The best flux estimates for DMS may hence be derived by adjustment of the flux value after attaining the optimal condition under which the differences can be minimized between the model-predicted and observed DMS profile. (The minimization routine used here was “chi-squared testing”.)

4. Conclusion

In order to investigate various facets of the natural sulfur cycle at Cheju island, we undertook the measurements of DMS and CS_2 during the intensive study period for the ACE-ASIA project in April 2001. As the measurements were made continuously at short-time intervals (i.e., 20 min), we were able to analyze the data sets in relation to other intensive measurements. Because the relative relationships of two S compounds were so distinctive across the whole measurement period (JD 95 ~ 116), all data sets were analyzed after sorting them into three different timeframes. Comparison of these data sets indicated that the distribution patterns for these S-gases between the different study periods were in general highly compatible with those derived concurrently for most of the relevant parameters. According to our data analysis, the distributions of both compounds exhibited large concentration variations across the three study periods defined. Whereas high concentrations of CS_2 (11.1 pptv) were prevalent during study period I, DMS concentrations showed the maximum mean values (22.3 pptv) during period III.

As seen from our present study, large temporal variabilities appear to exist in S gas distributions at the Kosan site in Cheju. According to our grouping of data sets into three defined study periods, the S gases concentrations varied in two distinctive ways. Despite the observed variabilities in their distributions, their temporal trends across different periods were in general compatible with the environmental

conditions that prevailed during each period. Although unusual seasonal weather patterns were seen for each period, the S gases data have been explained in relation to the environmental conditions. The overall results of our study suggest that the behavior of these S gases in the environment are affected by complicated source/sink processes which are highly variable compared to those which exist in remote oceanic environments.

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Figure Captions

Fig 1. The location of sampling station, Kosan district of Cheju Island in the southwest sea of the Korean Peninsula

Fig 2. A comparison of temporal distribution patterns of DMS and CS₂ determined at Cheju island for the whole study period of 5~26 April 2001. Arrows with dotted line are used to distinguish the three periods defined in this study (Julian day of 95 corresponds to Apr. 5, 2001.)

Fig 3. Results of linear regression analysis between DMS and CS₂ for all data and the three different study periods.

Fig 4. A comparison of temporal distribution trend of environmental parameters determined at Kosan, Cheju island during April 2001. Arrows with dotted line are used to distinguish the three periods defined

in this study (Julian day of 95 corresponds to Apr. 5, 2001.)

Fig 5. Results of back-trajectory analysis for the three different periods classified in this study.

Fig 6. A comparison of frequency distribution of windrose data sets among the three different study periods.

Fig 7. Diurnal variations of DMS and CS₂ are compared for all data sets and for the three different periods.